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FULL PAPER

Application of Si/SiC ceramic filters as support for structural palladium catalysts for the reductive decomposition of aqueous nitrite

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A Si/SiC ceramic filter was used to support a structural palladium catalyst in a continuous fixed-bed flow reactor during a reductive decomposition of nitrite. A previous report described the use of non-porous alumina spheres coated with Pd/C, a carbon monolith impregnated with Pd or a structural catalyst consisting of a polyurethane sponge skeleton impregnated with Pd resulted either in negligible activity or a complete stoppage of the flow by increasing the pressure drop in the flow system. The use of a Si/SiC filter impregnated with palladium, however, overcame the demerits and resulted in an 11% conversion of nitrite in 60 min. The use of a Si/SiC filter coated with a char intermediate followed by impregnation with Pd (Pd/C/Si/SiC) resulted in a structural catalyst that enhanced the activity to yield a 33% conversion of nitrite in 60 min. When five Pd/C/Si/SiC structural catalysts were used, however, the complete decomposition was achieved in the same amount of time. Although improvement was previously observed by using an alumina intermediate, use of the char intermediate resulted in a new factor for activity improvement. The characterization results show that it was the affinity between aqueous nitrite and the intermediate rather than palladium dispersion that contributed the most to the improvement of activity.

Key-words : Si/SiC ceramic filter, Reductive decomposition, Nitrite, Palladium, Char intermediate

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1. Introduction

In our laboratory, we examined a high-performance and continuous mass-processing system that uses a solid catalyst and is considered suitable for the recycling treatment of drinking water. To accomplish continuous and recycling mass processing of drinking water, Hayashi et al. conducted a preliminary experiment on the reductive decomposition of aqueous nitrite (NO_2^-) [Eq. (1)] via fixed-bed palladium catalyst systems composed of non-porous alumina spheres coated with Pd/C, a carbon monolith impregnated with Pd, or a structural catalyst consisting of a polyurethane sponge skeleton impregnated with Pd.[1)]

$$NO_2^- + 1.5H_2 \rightarrow 0.5N_2 + H_2O + OH^- \quad (1)$$

These attempts, however, resulted in unsuitable results such as serious pressure drops that stopped the flow.[1)] These preliminary experiments revealed that the most attractive issue in a continuous recycling system using a palladium catalyst must be a structural support rather than that of a monolith support, a sphere support, or a sponge skeleton.

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Under those circumstances, we focused on a Si/SiC filter as the structural support in our previous study.[2)] Values for porosity and bulk density of the filter were 95.6% and 0.12 g/cm^3, respectively. Therefore, the use of the filter was expected to result in a decrease in the pressure drop, which was expected to decrease the flow. Suitable flow was observed, however, when the Si/SiC was impregnated with palladium. Furthermore, improvement of the catalytic activity was evident using Si/SiC covered with an alumina intermediate followed by the impregnation with palladium.[2)] In those catalytic activity tests, suitable activity was obtained with a greater specific surface area and a higher dispersion of the palladium.[2)] In the present study, in order to determine other factors for enhancement of the decomposition activity, char was used instead of the alumina intermediate.

In 2014, the Ministry of Health, Labor and Welfare of Japan revised the water quality standards for the presence of aqueous nitrite in drinking water from 10 mg/L to less than 0.04 mg/L due to the poisonous nature of nitrite as a causative agent for methemoglobinemia,[3),4)] diabetes,[5)] and stomach cancer.[6)] It should be noted that the reductive decomposition of nitrate (NO_3^-) by Pd–Cu catalyst was extensively studied,[7),8)] while an accumulation of nitrite accompanying the decomposition sometimes pointed out

as a serious problem.[1),9)] Therefore we are focusing on the reductive decomposition of nitrite.

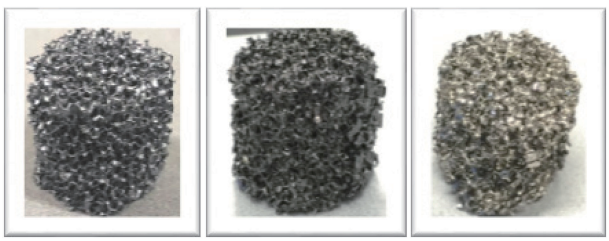
2. Experimental procedures

2.1 Preparation of structural catalysts

The structural support, used in the present study, was a Si/SiC ceramic filter (Si/SiC filter; #20, ϕ20 mm × 20 mm), acquired supplied from the Nippon Pillar Packing Co., Ltd. [**Fig. 1**(a)].

To use char instead of alumina as an intermediate (Pd/C/Si/SiC), a precursor of char was prepared by the polycondensation of resorcinol (Wako Pure Chemical Industries, Ltd.) and formaldehyde (Wako Pure Chemical Industries, Ltd.).[10)] An aqueous solution consisting of resorcinol (7.37 g; 66.9 mmol), 37% formaldehyde (10.0 mL; 134 mmol), potassium carbonate (Wako Pure Chemical Industries, Ltd.) (0.046 g; 0.33 mmol), and distilled water (23.31 g; 1.29 mol) was stirred at 298 K to obtain viscous resorcinol–formaldehyde sol (R–F sol). Into the R–F sol, a Si/SiC filter was dipped, dried at 353 K for 2 h and calcined at 1,073 K for 30 min at a rate of 10 K/min under an N_2 flow (30 mL/min) to form char-coated Si/SiC (C/Si/SiC) [Fig. 1(b)]. Aqueous $Pd(NO_3)_2$ (24.41% by weight, N. E. Chem-cat Co.) was impregnated into the C/Si/SiC followed by drying at 353 K for 3 h and calcination at 473 K for 3 h. This impregnation process was repeated to control the Pd loading. After impregnation, formalin reduction was carried out at 347 K for 2 h, followed by drying at 343 K under atmospheric pressure for 24 h, and then drying at 347 K for 24 h under vacuum. The resultant catalyst [Fig. 1(c)] was expressed as Pd(x)/C/Si/SiC with x as the impregnation time. The average loading of char (C) in Pd(x)/C/Si/SiC was 56.5 + 2.8%. For the reference, Si/SiC impregnated with Pd [Pd(x)/Si/SiC; x = impregnation time] and Si/SiC coated with alumina followed by the impregnation of palladium [Pd(x)/Al_2O_3/Si/SiC; x = impregnation time] were also used in the present study. The latter structural catalysts were prepared according to the procedure described in our previous paper.[2)]

The structural catalysts thus prepared were characterized using X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.), N_2 adsorption–desorption measurement (BELSORP-max12, MicrotracBEL Co.), CO pulse (BELCAT II, MicrotracBEL Co.) and scanning electron microscopy together with energy dispersive X-ray spectroscopy (SEM and EDX; JSM-6510A, JEOL ltd.). Monochromatized Cu Kα radiation (45 kV, 150 mA) was used for the XRD analysis. Prior to the N_2 adsorption–desorption measurement at 77 K, the catalysts were pretreated at 473 K for 5 h under vacuum. The loading of Pd was analyzed using ICP-AES (SPS3520UV, SII Nanotechnology Inc.) following the complete dissolution of Pd from the structural catalysts using aq. HNO_3.



(a) (b) (c)

Fig. 1. Photo images of (a) Si/SiC, (b) C/Si/SiC and (c) Pd(2)/C/Si/SiC.

2.2 Catalytic activity testing

Reductive decomposition of aqueous nitrite was examined in a continuous recycling apparatus using a fixed-bed structural palladium catalyst.[2)] Aqueous nitrite (100 ppm $NaNO_2$ solution: 0.87 mmol/400 mL) was added to a 4-necked flat-bottom separable flask that was connected to a hydrogen gas-holding, 0.25 M HCl burette in order to adjust pH = 6 of the aqueous solution, the electrode, and the catalyst bed. It has been already reported that the decomposition via zero or first order proceeded at pH = 5–7 or 8, respectively, using a batch systm.[1)] In order to achieve the complete decomposition of nitrite, the solution pH was adjusted to 6 that was suitable for zero order decomposition. A given number from 1 to 5 of the structural catalysts were put into the catalyst bed, which allowed solution to flow from bottom to top. The reaction temperature was controlled using double thermostatic baths adjusted to 298 K. In this operation, a solution of aqueous nitrite saturated with hydrogen via the use of a magnetic stirrer was supplied to the catalyst bed and recycled using a pump. Unless otherwise stated, the flow rate was set either at 572 or 478 mL/min for one or five filters. The higher flow rate employed either one or five filters at either 1,166 or 1,048 mL/min, respectively. Both the nitrite concentration and the hydrogen volume consumed in the decomposition were monitored. An aliquot of the liquid sample was taken intermittently using a sampling syringe for analysis of the nitrite composition via ion-chromatography (DKK-TOA Co., PCI-230). The concentration of NH_4^+ was monitored via indophenol blue method using an ultraviolet–visible spectrophotometer [UV-2,500(PC)S, Shimadzu Co].[11)]

3. Results and discussion

3.1 Effect of char intermediate on the decomposition of nitrite

In our previous study,[2)] we described a structural catalyst prepared via the impregnation of Pd onto Si/SiC (Pd/Si/SiC) and how it showed lower catalytic activity due to the low levels of loading and dispersion of Pd over a Si/SiC filter. Based on these results, we suggested the use of an intermediary between the filter and the Pd catalyst. Therefore, the advantageous effects of the char intermediate were examined by comparing the decomposition activity when using either Pd/Si/SiC or Pd/C/Si/SiC.

As shown in **Fig. 2**, when one structural catalyst was set in the catalyst bed, the conversions of nitrite using Pd(5)/Si/SiC and Pd(1)/Si/SiC were 11% regardless of the

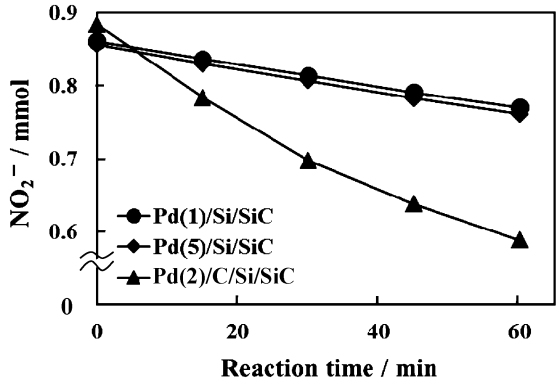


Fig. 2. Effects of char intermediate on the decomposition of nitrite using a Pd catalyst.

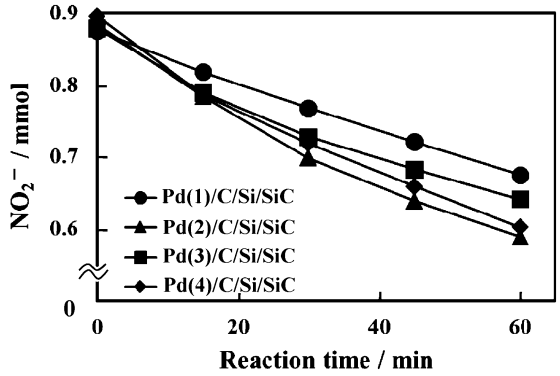


Fig. 3. Effects of the impregnation times of Pd onto char-coated Si/SiC on the decomposition of nitrite using a Pd/C/Si/SiC catalyst.

impregnation times of Pd onto Su/SiC. When Pd(2)/C/Si/SiC was used, however, a 33% conversion of nitrite was observed. This showed that the char intermediate enhanced the impregnation of Pd on the surface.

In order to adjust the impregnation time of Pd, several samples of Pd/C/Si/SiC were prepared using various impregnation times of Pd for the reductive decomposition of nitrite. As shown in **Fig. 3**, the best decomposition activity was detected when using the char-coated structural catalyst impregnated twice with Pd. This level of catalytic activity was reproduced even though the structural catalyst was used repeatedly (not shown). Therefore, the remainder of the present manuscript will describe the results using Pd(2)/C/Si/SiC. Since the decomposition of nitrite was not complete using one structural catalyst, Pd(2)/C/Si/SiC, a plurality was employed.

As shown in **Fig. 4**, an increase in the number of catalysts from one to five, that is, a decrease of space velocity (flow rate/volume of the structural catalyst) from 4,570 to 910 h^{-1}, led to an evident improvement in the catalytic activity from 0.30 to 0.74 mmol/h of the nitrite converted. The complete decomposition of nitrite was observed when using five structural catalysts of Si/SiC covered with an alumina intermediate followed by impregnation with palladium [Pd(5)/Al_2O_3/Si/SiC][2] at a flow rate of 1,048 mL/min. A complete decomposition was not detected,

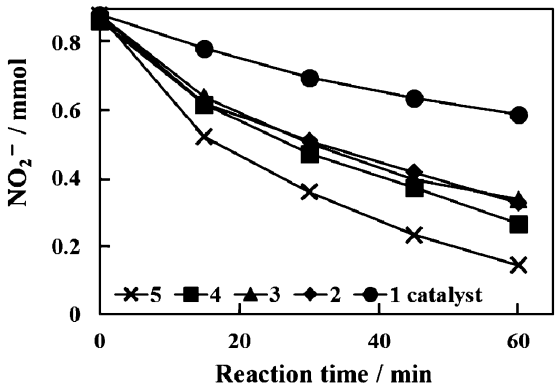


Fig. 4. Effects of the number of the structural catalyst, Pd(2)/C/Si/SiC, on the decomposition of nitrite.

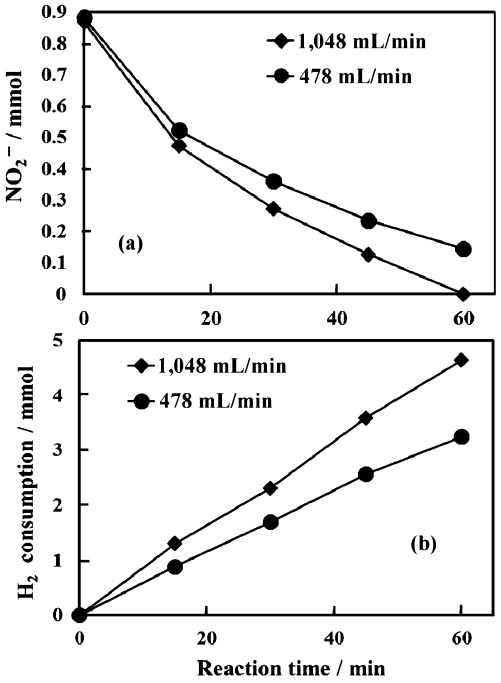


Fig. 5. Effects of the flow rate of aqueous nitrite on the decomposition of nitrite using a Pd(2)/C/Si/SiC.

however, even when five Pd(2)/C/Si/SiC catalysts were used at a lower flow rate of 478 mL/min.

Therefore, we accomplished a complete decomposition of nitrite using five Pd(2)/C/Si/SiC at 1,048 mL/min, as shown in **Figs. 5**(a) and 5(b) for nitrite concentration and hydrogen consumed, respectively. The higher flow rate of aqueous nitrite reduced the space time of the aqueous solution with the structural catalyst, but the recycling time of the aqueous nitrite with the structural catalyst was enhanced. Furthermore, sufficient dissolution of gaseous hydrogen into hydrogen-deficient aqueous nitrite following contact with the catalyst was quickly repeated to enhance the decomposition activity to show the results in Fig. 5.

Based on these results and the employment of pH = 6, the latter of which is suitable for the complete decomposition of nitrite, this system is expected to clear the

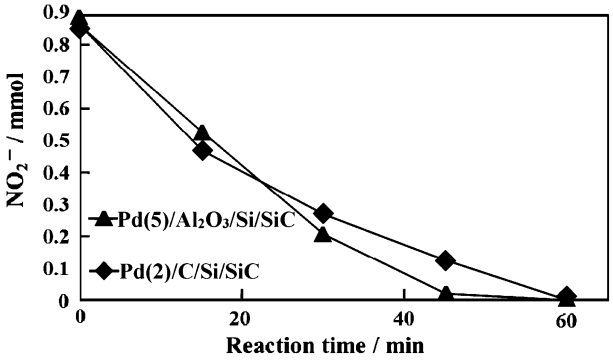


Fig. 6. Decomposition activity of nitrite using five structural catalysts of Pd(2)/C/Si/SiC and Pd(5)/Al_2O_3/Si/SiC at a flow rate of 1,048 mL/min.

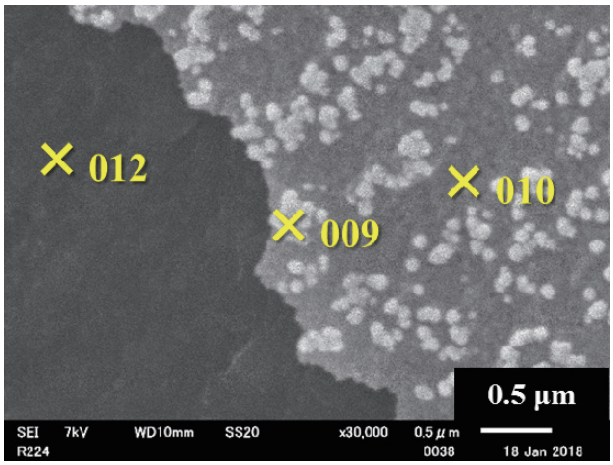


Fig. 7. SEM image of a Pd(2)/C/Si/SiC.

water quality standard on nitrite. It should be noted that molar number of hydrogen consumption was approximately five times greater than that of NO_2^- decomposed. As described below, NO_2^- was converted to various by-products together with N_2.[12] However the consumption amount of hydrogen was evidently greater than that expected from the reactions. This shows that hydrogen may be used for the redox of Pd catalysts together with the reductive decomposition.

The decomposition activity using five Pd(2)/C/Si/SiC catalysts was essentially identical to that using five Pd(5)/Al_2O_3/Si/SiC catalysts (**Fig. 6**). This proved to be the most important result, as discussed below.

Next, we focused on the formation of by-products. Hayashi et al. reported the formation behavior of by-products obtained from the reductive decomposition of aqueous nitrate on a Cu/Pd/C powder catalyst using a batch reactor system at 293 K.[1] With a shorter reaction time of 30 min, NO_2^- and N_2O were detected together with N_2 at molar ratios of $NO_2^-/N_2 = 2.5$ and $N_2O/N_2 = 0.75$, and no formations of either NH_4^+ or NH_2OH were confirmed. The formation rate of NH_4^+, however, was extremely enhanced at 120 min. Molar ratios of $NO_2^-/N_2 = NH_4^+/N_2 = 1.4$ and $N_2O/N_2 = 0.53$ were detected in the aqueous reaction after 120 min of decomposition reaction time with no formation of NH_2OH. For both amounts of reaction times, the nitrogen mass balance was almost 100%. These results suggest that the most possible by-product should be NH_4^+. A recent study has shown, however, that NH_4^+ from nitrite hydrogenation on a Pd catalyst doped on alumina proceeds due to a unique interaction between unreactive nitrogen atoms and Pd species in a semi-batch system.[13]

We expected the formation of NH_4^+ to be suppressed when using the continuous recycling apparatus since a higher flow rate, equal to a shorter residence time in the recycling system, which may have been an important factor in the suppression of a deep reduction from nitrite to ammonium ion, which requires an excess amount of hydrogen, compared with the decomposition of nitrite to N_2.

$$NO_2^- + 3H_2 \rightarrow NH_4^+ + 2OH^- \quad (2)$$

Furthermore, an earlier report showed that NH_4^+ was produced during longer reaction times when using a batch reactor.[1] Therefore, an adjustment was made to prevent the formation of NH_4^+ via the deep reduction, which suggested the need for an adjustment to a shorter residence time. In order to confirm this, the NH_4^+ concentration obtained after the reductive decomposition of aqueous nitrite was analyzed using three Pd(2)/C/Si/SiC catalysts at 478 mL/min. Fortunately, only a small selectivity to ammonium cation (1.4%) was detected. Therefore, the use of the structural support of Si/SiC in order to avoid pressure loss from the continuous flow of aqueous nitrite may play an important role in the suppressing the formation of NH_4^+. Detailed study on the formation of NH_4^+ via the reductive decomposition of aqueous nitrite is now in progress.

3.2 Characterization of Pd(2)/C/Si/SiC

Since Pd(2)/C/Si/SiC showed the most suitable decomposition activity in the present study, this structural catalyst was characterized using various techniques. Results obtained via the similar analyses for Pd(5)/Al_2O_3/Si/SiC has been reported in our previous paper.[2]

XRD of the structural catalyst detected various peaks due to the Si (PDF 00-005-0565) and SiC (PDF 01-075-0254), while peaks due to Pd species were not detected. In order to detect the Pd species, Pd(2)/C/Si/SiC was analyzed using SEM-EDS.

Figure 7 shows an SEM image of the catalyst. In contrast to Pd(5)/Al_2O_3/Si/SiC,[2] an uniform image was not detected in the SEM. The surface consisted of three parts: 009 particles, a 010 layer, and a 012 layer. Therefore, these three parts were qualitatively analyzed via EDS (**Fig. 8**). All the parts showed negligible peak intensity due to Si and evident peak intensity due to C, which indicated that Si/SiC was well coated by the carbon species, char. It is noteworthy that palladium was not detected on the 012 layer, and the strongest peak intensity due to Pd was detected on the 009 particles. Therefore, it may be concluded that less Pd was dispersed onto the C/Si/SiC. This

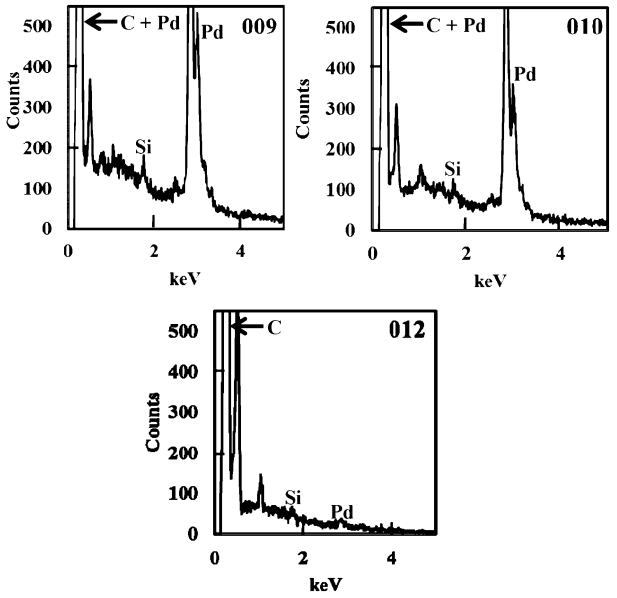


Fig. 8. Results of EDS spot analysis for 009 particles of 009, 010 layer, and 012 layer in Fig. 6.

Table 1. Pd loading, Pd dispersion, average particle size, and specific surface area of the structural catalysts

Catalyst	Pd loading /wt%	Pd dispersion /%	Average particle size /nm	Specific surface area /m^2/g
Pd(2)/C/Si/SiC	0.55	9.94	11.2	8.2
Pd(5)/Al_2O_3/Si/SiC	0.64	0.17	6.4	~0

situation was completely different from that on Pd(5)/Al_2O_3/Si/SiC, on which a greater dispersion of Pd was detected with SEM. In order to check the Pd dispersion on the surface, Pd(2)/C/Si/SiC was further analyzed using a CO pulse method for Pd dispersion and N_2 adsorption–desorption measurement for a specific area of the surface.

Table 1 shows the Pd loading, Pd dispersion, average particle size, and specific surface area of Pd(2)/C/Si/SiC and Pd(5)/Al_2O_3/Si/SiC, and the decomposition activity for both is described in Fig. 6. Since the loading of Pd in both structural catalysts was similar, it would be reasonable to expect similar activity for the decomposition of nitrite, as shown in Fig. 5. The Pd dispersion and the specific surface area of Pd(2)/C/Si/SiC were evidently inferior to the values measured for Pd(5)/Al_2O_3/Si/SiC. Under these situations, the catalytic activity on Pd(5)/Al_2O_3/Si/SiC usually exceeds that on the activity on Pd(2)/C/Si/SiC, in contrast to the results shown in Fig. 6. It should be noted that, if the affinity between nitrite and char is superior to that between nitrite and Al_2O_3, the results in Fig. 6 should be reasonable.

4. Conclusions

In order to suppress the disadvantage of pressure loss for a continuous-flow system using a solid catalyst, a Si/SiC filter was used as a structural support for the reductive decomposition of aqueous nitrite. A structural palladium catalyst was prepared by covering the filter with char followed by an impregnation of palladium, which allowed a suitable continuous flow that accomplished a complete decomposition of aqueous nitrite within one hour at 298 K. Furthermore, use of the present structural catalyst prevented the formation of ammonium ion, which normally a frequent problem for this form of decomposition. Since most of the filter was covered with char, the specific surface area of the structural catalyst was negligible. Although palladium was supported on the catalyst surface at a comparatively lower level of dispersion, the above-mentioned effective decomposition was probably due to better affinity between the char and the nitrite. Finally it is worthwhile to mention that structural palladium-based catalyst in a continuous fixed-bed flow reactor during a reductive decomposition of nitrite can be applied to the reductive decomposition of nitrate using advanced catalytic procedures.[14)]

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References

1) H. Hayashi, S. Sugiyama, Y. Nomura and T. Yamazaki, Conference Proceedings of 10th Asian Pacific Confederation of Chemical Engineering, 1P-06-023, Fukuoka, Japan (2004).
2) S. Sugiyama, N. Fukushima, Y. Tsuchiya, M. Katoh, Y. Hayashi, Y. Arai and M. Akamatsu, *J. Chem. Eng. Jpn.*, 51, 83–88 (2018).
3) V. Y. Titov and Y. M. Petrenko, *Biochemistry (Mosc.)*, 70, 575–587 (2005).
4) M. T. Gladwin, R. Grubina and M. P. Doyle, *Accounts Chem. Res.*, 42, 157–167 (2009).
5) G. G. Dahlquist, L. G. Blom, L.-Å. Persson, A. I. M. Sandström and S. G. I. Wall, *Brit. Med. J.*, 300, 1302–1306 (1990).
6) N. S. Bryan, D. D. Alexander, J. R. Coughlin, A. L. Milkowski and P. Boffetta, *Food Chem. Toxicol.*, 50, 3646–3665 (2012).
7) Y. Sakamoto, M. Kanno, T. Okuhara and Y. Kamiya, *Chem. Lett.*, 125, 392–395 (2008).
8) M. A. Hasnat, I. Ishibashi, K. Sato, R. Agui, T. Yamaguchi, K. Ikeue and M. Machida, *Bull. Chem. Soc. Jpn.*, 81, 1675–1680 (2008).
9) Y. Sakamoto, K. Nakata, Y. Kamiya and T. Okuhara, *Chem. Lett.*, 33, 908–909 (2004).
10) T. Horikawa, J. Hayashi and K. Muroyama, *Carbon*, 42, 169–175 (2004).
11) Japanese Industrial Standards Committee, *JIS K 0102:2013*, p. 151.
12) Y. Wang, Y. Sakamoto and Y. Kamiya, *Appl. Catal. A-Gen.*, 361, 123–129 (2009).
13) Y. Zhao, N. K. Rao and L. Lefferts, *J. Catal.*, 337, 102–110 (2016).
14) J. Hirayama and Y. Kamiya, *J. Catal.*, 348, 306–313 (2017).